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Epitaxial Growth and Electro-Optical Properties  
of Metal GaAs Superlattices

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# Epitaxial Growth and Electro-Optical Properties of Metal GaAs Superlattices

The objective of this research program is to investigate the metal systems that are thermodynamically stable on GaAs. Moreover, for novel device applications, the metal films should be epitaxial on GaAs, and that means the lattice mismatch between metal and GaAs should be as small as possible. From this stable metal contacts, we can then explore new properties and physics of the metal/GaAs heterojunction. Furthermore, new metal quantum well and superlattice devices can be fabricated, and a new generation of detectors and devices with improved performance will emerge.

The theoretical calculation of the metal quantum well (QW) photodetector has shown that the device can be served as a long wavelength (infrared) detector with an absorption efficiency one order of magnitude higher than a semiconductor QW device (e.g., AlGaAs/GaAs/AlGaAs). This enhancement is due to the higher oscillation strength of the metal intersubband transition. Furthermore, the selection rule governing the absorption of radiation by semi-metal QW yields a maximum transition probability for normal incidence. In this case, larger area devices or detector array can be fabricated. Using the band alignment concepts, we can make possible the infrared detectors and sources capable of tuning the detecting and radiating wavelength.

The key issue in realizing the QW structure is to make sure that the epitaxial metal film does not react chemically with the GaAs substrate during growth of the alternating layers. The novel approach initiated in this research is to utilize the intermetallic compounds. From the study of the bulk metal-GaAs reaction, we find  $\text{PtGa}_2$  and  $\text{CoGa}$  to be promising materials. These compounds have small lattice mismatches with GaAs (half of the lattice constant) and they both have cubic crystal structures. From the bulk ternary phase diagrams, they are both thermodynamically stable with GaAs. Two different techniques are used for growing these metal films on GaAs, i.e., MBE (molecular beam epitaxy) and MOCVD (metal organic chemical vapor deposition). Single phase  $\text{PtGa}_2$  and  $\text{CoGa}$  on GaAs can be obtained by both methods.

Successful growth of the single phase PtGa<sub>2</sub> and CoGa is demonstrated by MOCVD using mixed-metal organometallic precursors of limited volatility. The desired ligands have been developed. New approach such as photo-assisted deposition is also under investigation. In the UV-assisted experiments, we demonstrated a selective seeds, and this suggested the possibility of selective growth and in-situ device



by Codes  
and/or  
Special

fabrication.

MBE growth of  $\text{PtGa}_2$  and  $\text{CoGa}$  is of more importance consequence during this reporting period because of its ability to obtain high quality epitaxial films. Different Pt-Ga compounds are grown on GaAs by changing the Pt-Ga flux ratio and the thermodynamic stability is probed by X-ray diffraction and RBS (Rutherford backscattering). Among these Pt-Ga compounds,  $\text{PtGa}$ ,  $\text{Pt}_2\text{Ga}$  and  $\text{PtGa}_2$ ,  $\text{PtGa}_2$  has the highest stability up to  $800^\circ\text{C}$  annealing. Therefore, we optimize the growth of  $\text{PtGa}_2$  and obtain a high quality single phase  $\text{PtGa}_2$  film. The electronic structure of the  $\text{PtGa}_2$  film is analyzed by X-ray photoemission spectroscopy. It is shown that for decreasing Pt concentration, the Pt d-band centroid moves to higher binding energy and the density of states (DOS) at the Fermi-level decreases. The electric resistivity of the Pt-Ga compounds and also the Schottky behavior of the  $\text{PtGa}_2$  diode are also investigated.

Compared with  $\text{PtGa}_2$ ,  $\text{CoGa}$  has several advantages that make it a better candidate for more extensive study. From the ternary phase diagram, Co-Ga has only two stable compounds with GaAs:  $\text{CoGa}$  and  $\text{CoGa}_3$ . Therefore, the deposition of single phase  $\text{CoGa}$  is much easier than  $\text{PtGa}_2$  where many phases were found in this course of study. Furthermore, the large range of stoichiometry of  $\text{Co}_x\text{Ga}_{1-x}$  ( $x$  between 0.4 and 0.6) also makes the flux control less critical. The lattice mismatch between  $\text{CoGa}$  and GaAs can be changed by the stoichiometry of  $\text{Co}_x\text{Ga}_{1-x}$ , and the mismatch with the 60% Ga ratio is only 0.8%. The occurrence of different epitaxial orientations is a common problem in the deposition of intermetallic compounds on GaAs (e.g.,  $\text{RhGa}$  and  $\text{NiAl}$ ). Two different orientations (100) $\text{CoGa}$  and (110) $\text{CoGa}$  on (100)GaAs are always observed in the beginning of our research. However, one of our major accomplishments is to control the orientations at will by the study of the initial surface condition. In that study, the initial growth conditions are determined by the in-situ RHEED (reflection high energy electron diffraction) pattern, and for Co-terminated surface, the orientation is (100) $\text{CoGa}/(100)\text{GaAs}$ . For Ga-terminated surface, the orientation is (110) $\text{CoGa}$ , and for As-terminated surface, the deposition is the mix of (100) and (110) $\text{CoGa}$ . The good quality of the epitaxial films is characterized by RHEED, RBS and X-ray rocking curve. Both the (100) and (110) $\text{CoGa}$  show a streaky RHEED patterns with clear Kikuchi bands. The RBS channeling minimal is only 8% and the FWHM (full width half maximum) of the X-ray rocking is only 0.2 degree.

Another accomplishment is to establish the stability of  $\text{Co}_x\text{Ga}_{1-x}$ . The relation between the thermodynamic stability and the different stoichiometric  $\text{Co}_x\text{Ga}_{1-x}$  is

investigated for the first time. The stability is determined by the occurrence of the  $\text{CoGa}_3$  phase upon annealing. We have shown that for Co-rich samples the reaction between CoGa and GaAs is below  $450^\circ\text{C}$ . However, for Ga-rich films, the stability is improved dramatically. For the 60% Ga ratio, the highest temperature we can have without reaction is up to  $800^\circ\text{C}$ .

We have demonstrated the successful growth of CoGa and  $\text{PtGa}_2$  which form chemical stable and epitaxial metal contacts on GaAs. They both show a sharp interface and good crystallinity up to  $800^\circ\text{C}$  annealing. These new metal/GaAs interfaces should form the basis for fabricating devices with outstanding survivability and stable electrical properties. Based on this exciting results, we are now pursuing the development of metal/GaAs superlattice and quantum well structures. These materials are expected to have unique electro-optical properties, in addition to excellent stability. Their applications will be in millimeter wave and infrared detectors as well as other high speed devices.

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- H. Kaesz: "Deposition of thin metal film by OMCVD," 3rd European Chemical Society Meeting, Sept. 25-29, 1989, Kolugstein, Frankfurt. West Germany.
- R. S. Williams: "Initial stage of metal/semiconductor interface formation," 3rd International Conference on Semiconductor Interface Formation. Takanazuka, Japan. Nov, 1989.

(b.) Contributed Presentations at Topical or Scientific/Technical Society Conferences

- L. P. Sadwick, K. L. Wang, D. L. Joseph, and R. F. Hicks: "In-Situ infrared spectroscopy of MBE grown GaAs," 9th MBE Workshop, Purdue Univ., Indiana, Sept. 21-23, 1988.
- H. D. Kaesz, R. S. Williams, T. A. Chen, Z. Xue, D. Zu, and D. K. Shuh: "Low temperature organometallic chemical vapor deposition of transition metals," MRS, April 1988.
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- L. P. Sadwick, R. M. Ostrom, B. J. Wu, K. L. Wang, and R. S. Williams: "Electrical and optical properties of thin intermetallic platinum gallium films grown by MBE on GaAs and Si," MRS, San Diego, Apr. 1989.
- D. Baugh, Y. K. Kim, and R. S. Williams: "Understanding the influence of interface properties and deposition parameters on the selective growth of (100) and (110)CoGa films on (100)GaAs," Material Research Society Fall Meeting, Boston, MA, Nov. 27-Dec.2, 1989.
- Y. K. Kim, D. Baugh, and R. S. Williams: "Thermodynamic phase stability on GaAs of the intermetallic thin film CoGa with a large range of compositions," Material Research Society Fall Meeting, Boston, MA, Nov. 27-Dec.2, 1989.
- L. P. Sadwick, Y. K. Kim, D. Baugh, and R. S. Williams: "Stability of the electrical properties of PtGa intermetallics on annealing conditions," Material Research Society Fall Meeting, Boston, MA, Nov. 27-Dec.2, 1989.
- R. S. Williams: "The quest for the ideal metal/semiconductor interface," Symposium for the Center for Surface and Interface Science, Irvine, CA, Sep. 1989.
- D. Baugh, Y. K. Kim, and R. S. Williams: "Understanding the influence of interface properties and deposition parameters on the selective growth of (100) and (110)CoGa films on (100)GaAs," Minerals, Metals and Materials Society Spring Meeting, Anaheim, CA, Feb. 19-23, 1990.
- D. Baugh and R. S. Williams: "Selective growth of (100) and/or (110)CoGa films on (100)GaAs," Gordon Research Conference on "Electronic Materials", Ventura, CA, Feb. 26-Mar. 2, 1990.
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- R. Arghavani, K. L. Wang, and G. Karunasiri: "Internal photoemission in CoGa/GaAs Schottky barriers, possible injection of electrons into X and L valleys," American Vacuum Society 37th Annual Symposium, Oct. 8-12, 1990, Toronto, Canada.
- H. Kaesz: "Deposition of thin metal film by OMCVD," 3rd European Chemical Society Meeting, Sept. 25-29, 1989, Kolugstein, Frankfurt, West Germany.
- R. S. Williams: "Initial stage of metal/semiconductor interface formation," 3rd International Conference on Semiconductor Interface Formation, Takanazuka, Japan. Nov, 1989.
- R. S. Williams: "The quest for the ideal metal/semiconductor interface," Symposium for the Center for Surface and Interface Science, Irvine, CA, Sep. 1989.

**(c.) Related Dissertations by Ph. D. Students**

- L. P. Sadwick:  
"Material and electrical characterization of Platinum-Gallium intermetallic contacts grown by MBE on GaAs." Ph.D. 1989.
- Y. K. Kim:  
"The chemical reactions at intermetallic compound/III-V compound-semiconductor interfaces and the valence band electronic structures of Pt-Ga intermetallic compounds," Ph.D. 1990.

# LOW-TEMPERATURE ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION OF TRANSITION METALS

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## ABSTRACT

A variety of transition-metal films have been grown by organometallic chemical vapor deposition (OMCVD) at low temperatures using hydrocarbon or hydrido-carbonyl metal complexes as precursors. The vapors of the metal complexes are transported with argon as the carrier gas, adding H<sub>2</sub> to the stream shortly before contact with a heated substrate.

High-purity platinum films have been grown using ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)PtMe<sub>3</sub> [1] or ( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)PtMe<sub>3</sub> [2] at substrate temperatures of 180°C or 120°C, respectively. The incorporation of a methyl substituent on the cyclopentadienyl ligand decreases the melting point of the organoplatinum complex from 106°C [1] to 30°C [2] and increases the vapor pressure substantially. Film deposition also occurs at a lower substrate temperature. Analyses by X-ray diffraction (XRD), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) indicate that the films are well crystallized and do not contain any observable impurities after sputter cleaning.

The substrate temperatures for the first appearance of other transition-metal films from organometallic precursors are as follows (°C): Rh( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> (120/Si), Ir( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> (100/Si), HRe(CO)<sub>5</sub> (130/Si) and Ni( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub> (190/glass, 280/Si). These films are essentially amorphous and contain trace oxygen impurities (< 2%), except for the Re film, which was 10% oxygen and 20% carbon.

## INTRODUCTION

Low-temperature deposition processes are desired for very large-scale integrated (VLSI) microelectronics to reduce wafer warpage, generation of defects, and redistribution of dopants(s). Organometallic chemical vapor deposition (OMCVD) often provides routes to desired materials at lower temperature than possible with corresponding inorganic precursors. The difficulties of deposition of most transition metals using CVD are, (a) the non-availability of volatile precursors and, (b) the high temperatures required to decompose the precursors. However, the possibilities of large throughput and good step coverage are so attractive that attempts continue to be made to find ways to deposit transition metals using OMCVD at low temperature.

## SELECTION OF SOURCE MATERIALS

Much of the previous work involved transition metal complexes of *acac* (acetylacetonate), carbon monoxide, halogens and/or PF<sub>3</sub> [1-5]. These precursors frequently led to incorporation of heteroatoms into the films, and otherwise unsuitable results. Based on earlier observations in this laboratory [6] and elsewhere [7,8] of the decomposition of metal carbonyl and/or hydrocarbon complexes under an atmosphere of hydrogen, we were prompted to examine such derivatives for OMCVD in the presence of H<sub>2</sub>. The complexes tested successfully and those that produced films with the smallest amounts of incorporated contaminants are presented in Table I.



# Laser-driven chemical vapor deposition of platinum at atmospheric pressure and room temperature from $CpPt(CH_3)_3$

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Photolysis of  $CpPt(Me)_3$  ( $Cp = \eta^5-C_5H_5$ ,  $Me = CH_3$ ) at room temperature and atmospheric pressure produces thin films and patterned structures of platinum metal on solid substrates. The platinum films are characterized by Auger electron spectroscopy, x-ray diffraction, and scanning electron microscopy. Substrates can also be prepatterned by laser irradiation and then developed into a shiny platinum deposit at a later time.

Thin films and patterned microstructures of platinum are of interest for applications to microelectronics because the metal has low resistivity and high stability. Thermal deposition of platinum from the vapor phase has been successful using  $Pt(\text{acetylacetonate})_2$ ,  $Pt(PF_3)_4$ , and  $Pt(CO)_2Cl_2$ .<sup>1-3</sup> However, relatively high temperatures were required (200–600 °C) and the deposits were contaminated by heteroatoms from the ligands. The air-stable organometallic platinum compound  $CpPt(Me)_3$  has a high vapor pressure (0.052 Torr at 20 °C)<sup>4</sup> and has recently been reported to yield high quality thermally deposited films at 250 °C and  $10^{-4}$  Torr.<sup>5</sup> Photolysis offers a promising method of producing thin films and especially patterned microstructures at temperatures much lower than those possible in pyrolysis.<sup>6</sup> Laser-induced chemical processing for microelectronics takes advantage of both the specificity of the laser-induced chemistry and the ability of laser light to confine the reactions to the irradiated regions.<sup>7</sup> We report here the room temperature atmospheric pressure photolysis of  $CpPt(Me)_3$  ( $Cp = \eta^5-C_5H_5$ ,  $Me = CH_3$ ) to produce thin films and patterned structures of platinum metal on solid substrates.

$CpPt(Me)_3$  was prepared by the published procedure.<sup>8</sup> Laser photolysis was carried out with the 308 nm line of a XeCl excimer laser and with the 351 and 364 nm lines of an argon ion laser. The irradiation was carried out in a glass flow cell with a quartz window. Crystals of the Pt compound in a small bulb were warmed to ~56 °C (approximate vapor pressure 0.33 Torr)<sup>9</sup> and transported to the cell by flowing Ar at a flow rate of 2 cc/s. Hydrogen gas was introduced to the cell in proximity to the laser beam. Gas flow was parallel to the surface of the substrate. All photolyses were carried out at atmospheric pressure with the laser beam perpendicular to the surface. The substrates used in these studies included glass, fused silica, sapphire (1102), Si (001), and GaAs (001). The single-crystal silicon wafers were degreased by immersion in trichloroethylene and then rinsed in methanol and de-ionized water. The wafer was then twice etched for 2 min in a 1:4 solution of 30% hydrogen peroxide and concentrated sulfuric acid, rinsed in de-ionized water and blown dry in nitrogen.

The absorption spectrum of  $CpPt(Me)_3$  in the gas phase is almost identical to that of the compound in cyclohexane solution.<sup>10</sup> The lowest energy band has  $\lambda_{max}$  at 288 nm with an extinction coefficient of  $2.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ . The extinction coefficients at the wavelengths of irradiation are

$1.6 \times 10^3$ ,  $2.2 \times 10^2$ , and  $5.8 \times 10^1 \text{ M}^{-1} \text{ cm}^{-1}$  at 308, 351, and 364 nm, respectively.

Photodeposition studies at 308 nm were carried out by irradiating a circle 1 mm in radius with 2.6 mJ/pulse at 10 Hz. Shiny deposits were formed in about 10 min. The resulting films were about  $10^3 \text{ \AA}$  thick. Under these conditions, the rate of deposition is on the order of 100 Å per minute. The films were shiny when hydrogen was present but black in the absence of hydrogen. Photodeposition under cw conditions was carried out with fluences of 4–5 mW/mm<sup>2</sup> at 351 and 364 nm. Under the same conditions of flow rates and temperatures as used above, visible films were formed in about 10 min. The shiny or black deposits were similar to those produced with the pulsed laser. Photolyses were attempted by using the visible lines (488 and 514 nm) from the argon ion laser. No deposits were formed with laser fluences as high as 0.5 W/mm<sup>2</sup>. These results suggest that the deposition process depends critically on the absorption of light and involves a photochemical process rather than solely resulting from local heating of the substrate. However, the overall mechanism may also involve surface adsorption of a photointermediate followed by thermal reactions on the surface (*vide infra*).

The platinum films were characterized by Auger electron spectroscopy (AES). The films were wiped with acetone to remove contaminants introduced subsequent to the deposition, allowed to dry, and loaded into a sample treatment chamber. The films were then transferred to the analy-

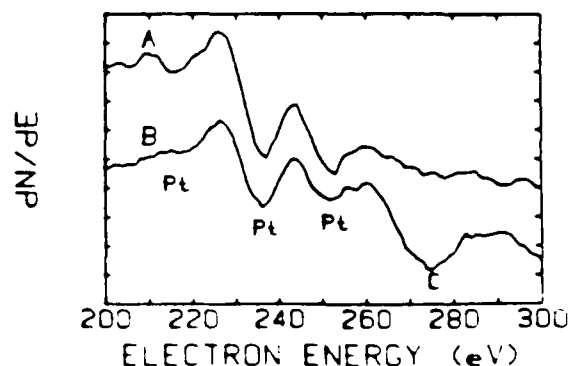


FIG. 1 Auger electron spectra of (A) a shiny deposit and (B) a black film collected with a hemispherical analyzer. The Pt peaks are at 217, 237, and 253 eV. The C peak is at 274 eV.

SURFACE SCIENCE LETTERS

**VIBRATIONAL SPECTRA OF HYDROGEN ATOMS ADSORBED  
ON MBE-GROWN GaAs(100)**

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Internal reflection infrared spectroscopy was used for the first time to observe the vibrational spectrum of H atoms adsorbed on GaAs(100) surfaces grown by molecular beam epitaxy. Initial H atom exposure produces one peak at  $2100\text{ cm}^{-1}$  due to an arsenic hydride species. With prolonged exposure, the  $2100\text{ cm}^{-1}$  vibration disappears and a second one appears at  $2140\text{ cm}^{-1}$  due to arsenic monohydride. Thus, for MBE-grown GaAs(100) only arsenic is accessible to the H atoms, and adsorption of H causes a change in the surface structure.

The interaction of gaseous atoms and molecules with compound semiconductors can dramatically affect the composition, structure, and electronic properties of their surfaces. Materials fabricated by molecular beam epitaxy (MBE) for metal-organic vapor phase epitaxy (MOVPE) grow from a surface exposed to gaseous species. The resulting film composition is a replica of the surface composition during growth. Moreover, the surface of the semiconductor exposed prior to deposition of a metal film becomes the active interface in an electronic device.

Hydrogen atoms strongly interact with GaAs surfaces at room temperature. Bartels et al. [1] found that H atom adsorption on cleaved GaAs(110) generates depletion layers in p- and n-type material which pin the Fermi levels at 0.63 and 0.85 eV above the valence band maximum, respectively. Thermal desorption spectroscopy of H from cleaved GaAs(110) reveals that  $\text{AsH}_3$  desorbs at room temperature [2]. Arsine continues to desorb with repeated adsorption-desorption cycles. Thus, the pinning of the Fermi level by H appears to be associated with the creation of arsenic defects.

There have been few studies of H atom interaction with MBE-grown GaAs(100) surfaces [3]. These surfaces are stabilized by arsenic. The As coverage of the top layer can vary from 100% to 30% depending on the extent

# In situ infrared spectroscopy of molecular-beam epitaxy grown GaAs

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Infrared spectroscopy of adsorbed molecules has been used to characterize semiconductor surfaces before, during, and after molecular-beam epitaxy growth. The technique relies on the principle of multiple internal reflections to enhance the weak response arising from the molecules adsorbed onto the semiconductor surface or trapped within the film. The resulting IR spectrum due to the adsorbed molecules provides detailed information about the chemical and physical structural bonding properties both within the epitaxial layer and at the semiconductor-vacuum interface. The experimental setup is compatible with UHV requirements and has been utilized in the pressure range from atmospheric down to the low- $10^{-10}$  Torr level.

## 1. INTRODUCTION

In the past few years, a large effort has been devoted to studying atomically clean semiconductor surfaces and the way in which the modification of such surfaces affects the material and electrical properties of devices fabricated on thin films grown on these surfaces.

In this paper, we discuss the use of infrared spectroscopy to characterize semiconductors during deposition by molecular-beam epitaxy (MBE) and chemical beam epitaxy (CBE). There are a number of excellent reviews on how to use this technique to study thin films and surfaces.<sup>1-4</sup>

We have recently reported the first observation of the vibrational spectrum of atomic hydrogen adsorbed on MBE grown GaAs.<sup>5</sup> Initial H atom exposure resulted in a peak at  $1100\text{ cm}^{-1}$  due to an arsenic hydride species. After prolonged H atom exposure, the vibrations due to the arsenic hydride disappeared and the arsenic monohydride (AsH) vibration is observed at  $2140\text{ cm}^{-1}$ . We have also investigated the incorporation of trimethyl gallium products during the growth of GaAs by MBE.<sup>6</sup> Moderate concentrations of trimethyl gallium led to extensive carbon incorporation. Absorbance at  $2950$ ,  $2925$ , and  $2855\text{ cm}^{-1}$  were observed almost instantly and continued to grow in intensity as the GaAs was deposited. These absorbance peaks have been attributed to the C-H stretch of  $\text{CH}_3$  and/or  $\text{CH}_2$  groups bonded to semiconductor atoms within the film. This undesirable carbon incorporation may be a significant consideration in the decision of whether trimethyl gallium is suitable as a gas source for chemical beam epitaxy.

There are basically two IR spectroscopy methods: the conventional external and the more elaborate attenuated total reflection. In essence, attenuated total reflection spectroscopy has a greater sensitivity and resolution.

This work discusses the use of *in situ* attenuated total reflection (ATR) spectroscopy for studying surface reactions in the initial stages of MBE growth and the impurity incorporation of the grown film.

## 2. EXPERIMENTAL METHOD

The ATR technique has submonolayer resolution, may be operated under any vacuum conditions including atmo-

spheric, and can assign the characteristic vibrational frequencies to various contaminants. The experimental configuration shown in Fig. 1 consisted of an ultrahigh vacuum GaAs MBE chamber which contained (among other components) Ga, As, and Si Knudsen cells surrounded by a liquid nitrogen cooled shroud, an electron gun (e-gun) for metal deposition, a quadrupole mass spectrometer, and entrance and exit optical windows for the IR beams. The entrance and exit optical windows are made of  $\text{CaF}_2$  mounted on a standard 2 in. diam. conflat flange. The IR beam is reflected by 2 4-in.-diameter mirrors and focused by a 2-in.-diam lens onto the sample in the vacuum chamber. A  $\text{CaF}_2$  lens with a cut-off wavelength of  $1100\text{ cm}^{-1}$  was used to focus the beam onto the total reflection element (IRE) entrance. The lens had a 240-mm focal length and was mounted at an angle of  $28.4^\circ$  from the horizontal to match the orientation of the UHV window. A Bio-Rad Digilab FTS-40 infrared spectrometer was used to provide the monochromatic exci-

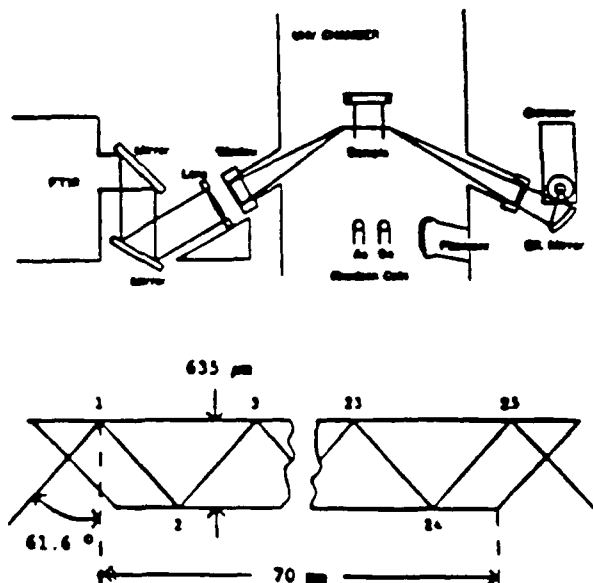


FIG. 1. *In situ* IR System and chamber and (b) internal reflection element (IRE).

# Theory and Applications of Band-Aligned Superlattices

KANG L. WANG, SENIOR MEMBER, IEEE AND PERNG-FEI YUH

**Abstract**—A general new device concept based on the miniband junctions formed in multiple superlattices is described. As heterojunctions play an important role in bulk semiconductor devices, the miniband junctions have potential applications for new superlattice devices. In the band-aligned structures, the aligned minibands function as an energy filter, which ensures efficient injection of monoenergetic carriers, while the miniband offsets can block the carrier flow similarly to the band discontinuity in bulk heterostructures. By engineering the alloy composition, the layer width, the doping, and the applied electric field, several examples of band-aligned superlattices are analyzed for applications in miniband transport and intersubband transitions.

## I. INTRODUCTION

ALMOST all of the semiconductor devices are made by doped p-n junctions and/or heterojunctions. Those junctions which make up the diverse device world have one thing in common; that is, they connect two semiconductor layers with different bands. The bands of a p-n junction are controlled by the dopants, while the bands of a heterojunction are changed by the alloy compositions.

The superlattice is made of periodic junctions such that the bands connected by the junctions form a one-dimensional periodic potential [1]. Because of this one-dimensional potential superimposed on the real crystal potential, minibands are formed within the conduction and valence bands. To explore the concept of semiconductor junction further, the question raised is what will be the junction which connects two superlattices having different minibands. By analogy with the junction devices, this new superlattice junction formed by stacking different types of superlattices can afford yet another dimension in the device world.

Usually, a superlattice is composed of a period of a simple element, e.g., square shape or a triangle potential. This, however, need not be the case. The building block of the superlattice can be any arbitrary potential well, and in addition, many different superlattices can be put together to form a device structure. We refer to the latter as a multiple superlattice, where "junctions" can be readily formed. The junctions between multiple superlattices can be divided into two categories: band alignment, where the minibands in both sides are partly or totally aligned, and

band offset or band stop, where the miniband on one side of the junction becomes an evanescent state on the other. For convenience, the name band-aligned superlattice (BAS) is used to refer to this new multiple superlattice [2], where the minibands are purposely aligned or not aligned, and a superjunction is the junction formed by such multiple superlattices.

The methods we use to investigate the BAS's are described in Section II. Several structures are analyzed with these methods in Sections III and IV for new infrared detector and laser applications.

## II. METHODS

For an ideal superlattice, where an infinite number of periodical layers is assumed, the Kronig-Penney model [3] can be used to determine the minibands and wave functions. For a finite superlattice, on the other hand, realistic calculations must be done for transmission coefficient and current, wave functions, and carrier density. The former model has been well established in the formulation of resonant-tunneling diodes [4], [5]. The latter has been developed previously by us [6] and also by some other authors in self-consistent calculations [7], [8]. However, all the previous formalisms consider only the energies above the conduction-band edge. For energies below the conduction-band edge, evanescent waves exist, and the carrier density due to these evanescent waves cannot be simply neglected, especially for the analysis of BAS's. Thus, in what follows, we will cite only the results for the oscillatory wave solutions and describe in detail the evanescent wave case. The GaAs/AlGaAs material system is used as an example in the following calculations, and extension to other semiconductor systems is straightforward.

### A. Transmission Coefficient and Current

Fig. 1 shows the conduction-band edge of a superlattice consisting of a finite number of layers with a total length  $L$ . The conduction-band envelope functions along the  $z$ -direction, denoted by  $\Psi_l$  and  $\Psi_r$  for the left- and right-hand contacts, respectively, are

$$\Psi_l = \begin{cases} A_+ e^{ik_l z} + A_- e^{-ik_l z} & \text{for oscillatory wave} \\ A_+ e^{k_l z} & \text{for evanescent wave,} \end{cases} \quad z \leq 0$$

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## LOW-TEMPERATURE ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION OF TRANSITION METALS

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### ABSTRACT

A variety of transition-metal films have been grown by organometallic chemical vapor deposition (OMCVD) at low temperatures using hydrocarbon or hydrido-carbonyl metal complexes as precursors. The vapors of the metal complexes are transported with argon as the carrier gas, adding H<sub>2</sub> to the stream shortly before contact with a heated substrate.

High-purity platinum films have been grown using ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)PtMe<sub>3</sub> [1] or ( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)PtMe<sub>3</sub> [2] at substrate temperatures of 180°C or 120°C, respectively. The incorporation of a methyl substituent on the cyclopentadienyl ligand decreases the melting point of the organoplatinum complex from 106°C [1] to 30°C [2] and increases the vapor pressure substantially. Film deposition also occurs at a lower substrate temperature. Analyses by X-ray diffraction (XRD), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) indicate that the films are well crystallized and do not contain any observable impurities after sputter cleaning.

The substrate temperatures for the first appearance of other transition-metal films from organometallic precursors are as follows (°C): Rh( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> (120/Si), Ir( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> (100/Si), HRe(CO)<sub>5</sub> (130/Si) and Ni( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub> (190/glass, 280/Si). These films are essentially amorphous and contain trace oxygen impurities (< 2%), except for the Re film, which was 10% oxygen and 20% carbon.

### INTRODUCTION

Low-temperature deposition processes are desired for very large-scale integrated (VLSI) microelectronics to reduce wafer warpage, generation of defects, and redistribution of dopants(s). Organometallic chemical vapor deposition (OMCVD) often provides routes to desired materials at lower temperature than possible with corresponding inorganic precursors. The difficulties of deposition of most transition metals using CVD are, (a) the non-availability of volatile precursors and, (b) the high temperatures required to decompose the precursors. However, the possibilities of large throughput and good step coverage are so attractive that attempts continue to be made to find ways to deposit transition metals using OMCVD at low temperature.

### SELECTION OF SOURCE MATERIALS

Much of the previous work involved transition metal complexes of *acac* (acetylacetonate), carbon monoxide, halogens and/or PF<sub>3</sub> [1-5]. These precursors frequently led to incorporation of heteroatoms into the films, and otherwise unsuitable results. Based on earlier observations in this laboratory [6] and elsewhere [7,8] of the decomposition of metal carbonyl and/or hydrocarbon complexes under an atmosphere of hydrogen, we were prompted to examine such derivatives for OMCVD in the presence of H<sub>2</sub>. The complexes tested successfully and those that produced films with the smallest amounts of incorporated contaminants are presented in Table 1.

# A STUDY OF THERMODYNAMIC PHASE STABILITY OF INTERMETALLIC THIN FILMS OF $\text{Pt}_2\text{Ga}$ , $\text{PtGa}$ AND $\text{PtGa}_2$ ON GALLIUM ARSENIDE

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## ABSTRACT

Epitaxial thin films of three different Pt-Ga intermetallic compounds have been grown on GaAs by molecular beam epitaxy (MBE). The resultant films have been annealed at various temperatures and then examined using X-ray two-theta diffraction. Both  $\text{PtGa}_2$  and  $\text{PtGa}$  thin films are chemically stable on GaAs under 1 atmosphere of  $\text{N}_2$  up to 450°C and 600°C, respectively. Thin films of  $\text{Pt}_2\text{Ga}$  react with GaAs at temperatures as low as 200°C to form phases with higher Ga concentration.

## Introduction

The interface chemistry of metal-semiconductor contacts plays an important role in controlling the electrical properties of Schottky barriers and Ohmic contacts [1]. Chemically stable contacts must be formed at the metal-semiconductor interface in order for electronic devices to survive processing procedures and operate reliably in harsh environment applications for long periods of time [2,3]. A possible solution for this interface problem would be to use a contact metal that can coexist with GaAs in bulk thermodynamic equilibrium. Such stable metals can be found by examining ternary phase diagrams, such as the Pt-Ga-As system, which was experimentally elucidated by Tsai et. al. [4] and is illustrated in Fig. 1. The existence of a pseudobinary tie-line between two compounds in the ternary phase diagram implies that the compounds will not react with each other in a closed system, i.e. the bulk compounds are in thermodynamic equilibrium with respect to each other. Therefore, from Fig. 1 it can be expected that  $\text{PtGa}$  and  $\text{PtGa}_2$  will form stable contacts with GaAs but that  $\text{Pt}_2\text{Ga}$  will not. In the present study, these expectations are tested by investigating the phase composition of thin films of  $\text{Pt}_2\text{Ga}$ ,  $\text{PtGa}$  and  $\text{PtGa}_2$  on GaAs after annealing to various temperatures.

## Film Growth

The Pt-Ga intermetallic films were grown in a MBE chamber with a base pressure of  $2 \times 10^{-10}$  torr and a deposition pressure of approximately  $4 \times 10^{-9}$  torr. The two inch GaAs substrates were introduced via a cryopumped load lock system and mounted on a modified manipulator equipped with radiative heating elements. The samples were cleaned in-situ by heating to a temperature of approximately 525°C. The platinum was evaporated using a Varian 3 KW electron beam evaporator and the gallium was obtained from a Knudsen cell constructed of a pyrolytic boron nitride (PBN) crucible with a tantalum heating element. The fluxes of platinum and gallium were initially tuned to the proper stoichiometry based on empirical knowledge.  $\text{PtGa}_2$  can be visually identified by its characteristic golden color, since  $\text{PtGa}_2$  is the only Pt-Ga phase that has a band structure similar to that of elemental gold [5]. Neither  $\text{PtGa}$  nor  $\text{Pt}_2\text{Ga}$  can be easily identified by color. The flux rate from the gallium source was stabilized by temperature control circuits that ensured a constant flux rate for each source power setting. Subsequent depositions have been controlled with a Leybold-Inficon IC-6000 crystal monitor system. To obtain single phase Pt-Ga intermetallic films, the flux ratio of gallium to platinum was adjusted to be slightly Ga rich. Co-evaporation of each Pt-Ga intermetallic proceeded with the substrate held at temperatures ranging from near room temperature to over 500°C at epilayer growth rates ranging from approximately 0.5 to 5 microns/hour.

## Composition Analysis

XRD patterns of the films were taken on a Phillips X-ray powder diffractometer, which was interfaced to a microcomputer that controlled the scan rate and collected data at  $0.1^\circ$  intervals with a counting time of 10 seconds at each angle. The total time required for a complete scan ( $2\theta$  from  $10^\circ$  to  $100^\circ$ ) was about 3 hours and the typical signal-to-noise ratio for a strong diffraction peak was 30 to 1. The d spacings of the  $\text{PtGa}_2$  and  $\text{Pt}_2\text{Ga}$  thin films were checked against a reference tabulation [6] to ensure that they were identified correctly. As

# ELECTRICAL PROPERTIES OF THIN INTERMETALLIC PLATINUM-GALLIUM FILMS GROWN BY MBE ON GALLIUM ARSENIDE AND SILICON

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## ABSTRACT

Thin films of the platinum-gallium (Pt-Ga) family have been grown on gallium arsenide (GaAs) and silicon (Si) by molecular beam epitaxy (MBE). A partial list of potential uses for these and similar structures is high temperature stable photodetectors, Schottky and Ohmic contacts, epitaxial buried contacts, and field effect transistors. In this work the electrical properties of Pt<sub>2</sub>Ga, PtGa, and PtGa<sub>2</sub> on both GaAs and Si will be presented. The resistivity of these thin films has been found to depend on the crystal quality and phase of the material.

## Introduction

Recently there has been a significant amount of interest in intermetallic compounds grown on GaAs [1,2,3]. Excellent properties have been obtained for CoGa grown on GaAs by Palmstrom et al. [2]. In this work we present the results of resistivity versus temperature for thin (~1000 to 2000 Angstrom) films of single phase Pt-Ga intermetallics grown at or near room temperature on GaAs(100) and Si(100). The resistivity versus temperature data was obtained using the van der Pauw method. A block diagram of the experimental setup is illustrated in Fig 1.

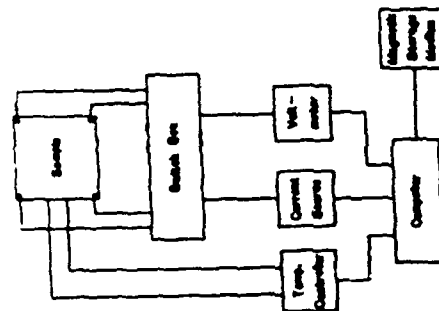


Fig. 1 Measurement setup.

## Characterization of (Methylcyclopentadienyl)trimethylplatinum and Low-Temperature Organometallic Chemical Vapor Deposition of Platinum Metal

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**Abstract:** ( $\eta^5$ -Methylcyclopentadienyl)trimethylplatinum, ( $\eta^5$ -MeCp)PtMe<sub>3</sub>, **1** (MeCp = CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>), is synthesized from trimethylplatinum iodide and sodium methylcyclopentadienide by the method of Fritz and Schwarzans. By using some care in the purification of bis(methylcyclopentadiene) from dicyclopentadiene, a sample of **1** is obtained showing a melting point of 29.5–30.0 °C and a vapor pressure of 0.053 Torr at 23 °C. <sup>1</sup>H and <sup>13</sup>C NMR spectra have been obtained, the latter both in solution as well as in the solid state. Coupling constants to the cyclopentadienyl ring carbons are found to differ, Hz: <sup>195</sup>Pt–<sup>13</sup>C<sub>Me</sub> = 13.62, while <sup>195</sup>Pt–<sup>13</sup>C<sub>H</sub> = 2.82 or 5.34. Five separate resonances are observed for the ring carbon atoms of the MeCp group in the solid state [<sup>1</sup>H]<sup>13</sup>C NMR. However, only one signal is observed at –73 °C or higher for the three methyl groups on Pt, indicating a low barrier for rotation of these groups in the solid state. The structure has been determined on a single crystal of **1** at –143 °C: monoclinic, space group P2<sub>1</sub>, with *a* = 7.159 (2) Å, *b* = 11.092 (3) Å, *c* = 6.004 (1) Å, and  $\beta$  = 106.806 (6)°. The structure was solved and refined by using 907 observed (*I* > 3 $\sigma$ (*I*)) independent reflections measured on a Picker automated diffractometer. Refinement uncorrected for absorption converged at *R* = 0.034 and *R*<sub>w</sub> = 0.060. The principal finding, of significance to the solid-state NMR, is the intermolecular contacts of 3.98, 4.55, and 4.94 Å between closest ring-carbon atoms on independent molecules in adjacent unit cells. These contacts are too close to permit rotation of the MeCp rings. The ring is pentahapto-bonded with almost identical Pt to ring-carbon distances within the limited accuracy of this determination, Å: C<sub>(Me)</sub>–Pt = 2.266, C<sub>(H)</sub>–Pt = 2.260, 2.314, 2.354, and 2.324. For deposition of metallic platinum, a stream of Ar gas at ambient pressure is first saturated with the vapor of **1** at 23 °C. This is then conducted into a chamber containing H<sub>2</sub> gas such that the ratio of saturated Ar:H<sub>2</sub> = 4:1. A substrate such as a glass slide or a Si(100) wafer, placed near the outlet of the saturated Ar gas stream and heated to 120 °C, becomes coated with a film of highly reflective Pt metal. The films have been characterized by powder X-ray diffraction (indicating a crystalline nature) and with X-ray photoelectron spectroscopy (XPS). A high purity, i.e., less than 1 atom % C, is indicated.

Thin films of platinum are used extensively in microelectronics device processing<sup>1,2</sup> and electrodeless metal plating.<sup>3</sup> Thermal deposition of platinum from the vapor phase has been reported with use of Pt(acetylacetonate)<sub>2</sub>, Pt(PF<sub>3</sub>)<sub>4</sub>, or Pt(CO)<sub>2</sub>Cl<sub>2</sub>.<sup>4–6</sup> These depositions require high temperature (200–600 °C), and the films are contaminated by heteroatoms from the ligands. We have been interested in finding other volatile organometallic compounds to obtain platinum films of higher purity. The ready decomposition of tris(ethylene)platinum was already known.<sup>7</sup> However, this hydrocarbon precursor is much too unstable for long-range storage and handling. Recently our group<sup>8</sup> and others<sup>9</sup> have reported organometallic chemical vapor deposition (OMCVD) from hydrocarbon precursors. In our work,<sup>8</sup> platinum films of high purity (>99 atom %) and high crystal quality were obtained at 180 °C from CpPtMe<sub>3</sub> (Cp = cyclopentadienyl) in the presence of H<sub>2</sub>. The need to have a liquid organometallic precursor for better control of evaporation has led us to investigate (methylcyclopentadienyl)trimethylplatinum, (MeCp)PtMe<sub>3</sub>, reported<sup>10</sup> to be an oily substance at room temperature. Here we report our studies on this complex. A preliminary account of a

part of this work has appeared.<sup>11</sup>

### Experimental Section and Results

**Preparation of (MeCp)PtMe<sub>3</sub>.** I. Commercially available bis(methylcyclopentadiene) (Aldrich) is only 95% pure. The dimer is thermally

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# Chemical vapor deposition of CoGa and PtGa<sub>2</sub> thin films from mixed-metalorganometallic compounds

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A new process for deposition of thin metal films from organometallic precursors of limited volatility has been demonstrated. Short path vapor transport of the complexes dichloro(tetracarbonylcobalt)gallium(III) tetrahydrofuranate, (CO)<sub>4</sub>CoGaCl<sub>2</sub>(THF), or platinum(bis-dimethylglyoximate)(bis-dimethylgallium), Pt{(N<sub>2</sub>C<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>O<sub>2</sub>)(GaMe<sub>2</sub>)<sub>2</sub>}, each under a stream of hydrogen, leads to the films of the intermetallic compounds CoGa and PtGa<sub>2</sub>, respectively, on substrates such as Si (100) wafer or a glass slide at 500 °C. The compounds were identified and characterized by x-ray diffraction, Auger electron and x-ray photoelectron spectroscopies. The films are crystalline and highly reflective. The CoGa film is single phased; the PtGa<sub>2</sub> film shows a minor constituent of Pt<sub>2</sub>Ga<sub>3</sub>.

Metal-semiconductor interfaces to form active Schottky barriers or Ohmic contacts are essential for solid-state circuits.<sup>1</sup> Whether a good Ohmic contact to III-V semiconductors can be achieved depends on the properties of the materials deposited on the surface of the semiconductors and the process of the contact formation. The formation of the contact should not undergo excessive high-temperature annealing because III-V semiconductors are unstable under heat treatment.<sup>2</sup> Schottky barrier gates require a reasonably large barrier height and good thermal stability during the temperature cycle for the subsequent source/drain Ohmic contact formation. Most elemental metals are chemically reactive on III-V semiconductor surfaces.<sup>2</sup> However, certain intermetallic compounds of transition metals and group III metals have been found to be thermodynamically stable on the III-V surfaces.<sup>3</sup> Currently, the deposition of thin films of intermetallic compounds involves coevaporation of the elements from separate sources in a vacuum chamber.<sup>4,5</sup> The primary difficulty with this approach is that the desired metal ratios are difficult to control.

Recently, we<sup>6</sup> and others<sup>7</sup> have shown that hydrocarbon complexes of transition metals are excellent precursors for thin metal films by low-temperature organometallic chemical vapor deposition (OMCVD); some of these films are obtained in unprecedented purity.<sup>6</sup> Deposition of organometallic complexes containing transition metals and group III metals in the ratio required for a particular stoichiometric intermetallic compound is of great current interest. The intermetallic compounds CoGa and PtGa<sub>2</sub> are particularly interesting because they form chemically very stable contacts on gallium arsenide.<sup>4,5</sup> However, previous attempts to form alloys via decomposition of mixed metal complexes have shown that it is difficult to maintain the original metal ratio in the film, especially when one component is volatile.<sup>8</sup> Here we report the formation of the first CoGa and PtGa<sub>2</sub> intermetallic compounds from mixed-metal organometallic precursors.

Very few organometallic compounds with the desired ratios of elements have thus far been reported.<sup>9</sup> For this study, we selected (CO)<sub>4</sub>CoGaCl<sub>2</sub>(THF) (THF = tetrahy-

drofuran), 1,<sup>10</sup> and Pt{(N<sub>2</sub>C<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>O<sub>2</sub>)(GaMe<sub>2</sub>)<sub>2</sub>}, 2,<sup>11</sup> structures of which are shown in Fig. 1.

These compounds have a very low vapor pressure at room temperature. Therefore, the depositions are carried out in a quartz combustion tube heated by a cylindrical furnace of known temperature profile; for this work we observed a Gaussian distribution beginning at 100 °C at the edge of the furnace when the maximum was at 500 °C in the center (for an overall furnace length of 40 cm). Solid samples of either 1 or 2 on a quartz boat were placed in a cool portion of the combustion tube and purged under a stream of hydrogen (20 ml/min) for 20 to 30 min. The sample holders were then pushed to a predetermined point to generate enough vapor pressure to be transported towards the substrates, i.e., 300 °C for 1, or 160 °C for 2. The substrates [Si (100) wafer or glass slide] were located near the center of the tube. The depositions were carried out over a 2 h period and the products obtained, namely, highly reflective films of CoGa or PtGa<sub>2</sub>, were identified and characterized by several means.

Power x-ray diffraction patterns (XRD) of the films were taken on a Philips diffractometer utilizing a Crystal Logic interface to a DEC VAX 11/750 mainframe computer. Diffraction patterns were obtained by accumulation of data for periods of time upwards of 12 h to achieve an ade-

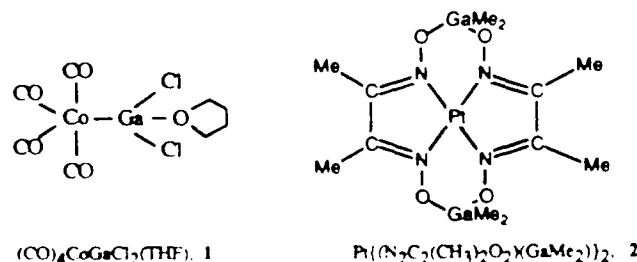


FIG. 1 Structures of dichloro(tetracarbonylcobalt)gallium(III) tetrahydrofuranate, 1, and platinum(bis-dimethylglyoximate)(bis-dimethylgallium), 2.

# DEPOSITION OF TRANSITION METAL AND MIXED METAL THIN FILMS FROM ORGANOMETALLIC PRECURSORS

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**ABSTRACT.** — A variety of transition metal films have been grown by (a) organometallic chemical vapor deposition (OMCVD), or (b) photo-assisted OMCVD of volatile hydrocarbon precursors, and (c) short-path OMCVD for organometallic precursors of limited volatility. High purity films have been grown for Re, Rh, Ir, Ni, and Pt under (a). Under (b), thin films have been grown of Pt, Rh, or Ir, however these contained somewhat greater carbon content than the films obtained under (a). The vapors of volatile hydrocarbon derivatives are transported with argon as carrier gas to selected substrates either (a) being heated to temperatures of 100 to 300° C, or (b) being irradiated using several different light sources. Hydrogen gas is introduced into the reaction chamber such that the ratio of sample-saturated Ar carrier gas to H<sub>2</sub> is 1:1 at the substrate. Kinetic studies on mixtures of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)PtMe<sub>3</sub> and H<sub>2</sub> reveal an induction period before measurable amount of surface reaction takes place; the reaction is catalyzed by deposited metal.

Procedure (c) has been employed for the deposition of films of the intermetallic compounds CoGa and PtGa<sub>2</sub>. A reaction tube of known thermal gradient is employed and hydrogen gas is also present. Mixed-metal precursor complexes were found to have less than 10<sup>-2</sup> Torr vapor pressure at room temperature. Such complexes are placed in a ceramic boat in the reaction tube at a point where sufficient vapor pressure is developed for transport. Substrates to be coated are placed further along the reaction tube at the temperature required for controlled decomposition of the precursor complexes. The resulting CoGa and PtGa<sub>2</sub> films have been analysed by X-ray diffraction, Auger electron spectroscopy and X-ray photoelectron spectroscopy (XPS).

## Introduction

This is an account of a collaborative effort among workers in several disciplines beginning with organometallic synthesis and thermal vapor deposition in my group (Dr. Yea-Jer Chen, Dr. Hans-Joachim Müller, Ziling Xue and Daqiang Xu), proceeding to photo-assisted OMCVD in collaboration with my colleague J. I. Zink, evaluation of the thin films by R. S. Williams and his students (David Shuh and Young Kwan Kim), and kinetic studies of the thermal deposition in collaboration with R. F. Hicks of the Chemical Engineering Department.

The selective deposition of metal films of high purity is of vital importance in integrated circuits<sup>1,2</sup>. Chemical vapor deposition (CVD) is often the method of choice for such applications compared to physical methods of deposition such as sputtering or evaporation under ultra high vacuum (molecular beam epitaxy)<sup>1,2</sup>. The advantages of CVD are selectivity, conformal step coverage, radiation damage-free deposition, high throughput, and low-cost<sup>1</sup>. These factors also make CVD more suited for industrial production<sup>2</sup>.

## Thermal Deposition of Thin Films of Platinum

The need for improved precursors for the CVD of platinum was indicated to us in the published work summarized in

Table I<sup>3</sup>. The temperatures required for these depositions were relatively high (200-600° C) and the films obtained were contaminated by heteroatoms from the ligands.

Table I. — Previous studies of chemical vapor deposition of platinum<sup>4</sup>.

Precursor	Source temp (°C)	Deposition temp (°C)	Comments
Pt(acac) <sub>3</sub> <sup>5</sup>	150	550	lots of carbon
Pt(CO) <sub>2</sub> Cl <sub>2</sub>	125	400	wrinkled, non-adherent film
Pt(PF <sub>6</sub> ) <sub>4</sub>	25	250	5% phosphorus

\* See ref. 3.

<sup>5</sup> acac = acetylacetonate, CH<sub>3</sub>C(O)CHC(O)CH<sub>3</sub>.

We were aware of the ready decomposition of tris(ethylene)platinum<sup>4</sup>, which complex was discovered after the above-mentioned studies had appeared. This compound is stable only under an atmosphere of ethylene and readily deposits platinum if the pressure of ethylene is removed and/or reduced. We were interested to find a hydrocarbon complex with somewhat better thermal and chemical stability. The studies of Egger<sup>5</sup> on ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)PtMe<sub>3</sub><sup>6</sup> offered a promising lead. Egger reported that "gaseous trimethylcyclopenta-

# Structural and chemical stability of thin films of Pt-Ga intermetallic compounds of GaAs(001)

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Nearly single-phase thin films of three different Pt-Ga intermetallic compounds have been grown on GaAs(001) by co-deposition of Pt and Ga. The resultant films have been annealed at various temperatures and then characterized using x-ray two-theta diffractometry (XRD), Auger electron spectroscopy (AES), and x-ray photoemission spectroscopy (XPS). The XRD results showed that PtGa<sub>2</sub> and PtGa thin films are chemically stable on GaAs under one atmosphere of N<sub>2</sub> up to 800 °C and 600 °C, respectively, but thin films of Pt<sub>2</sub>Ga react with GaAs at temperatures as low as 200 °C to form phases with higher Ga concentration PtAs<sub>2</sub>. The XRD patterns also revealed that the crystallite orientation and texture of the films were dependent on annealing temperature. Segregation of Ga to the surfaces of the films upon annealing was also observed by both AES and XPS. The results demonstrated that the as-deposited films of PtGa<sub>2</sub> and PtGa were kinetically stabilized with respect to possible chemical reactions with the GaAs substrates that evolve gaseous As species during open system annealing.

## I. INTRODUCTION

The metal/compound-semiconductor interface has attracted great interest because of the contact problem in microelectronic devices.<sup>1</sup> Many experimental and theoretical investigations have focused primarily on the electronic structure at the metal/semiconductor interface. The role that interfacial chemical reactions may play in determining the electrical properties of Schottky and ohmic contacts has been a subject of intense investigation and debate.<sup>2</sup>

The chemistry of contacts on compound semiconductors is intrinsically more complex than those on Si, because the presence of an additional element adds another degree of freedom to the phase diagram.<sup>3,4</sup> Thus, in general it is not possible to form a single phase contact to a compound semiconductor by simply depositing a film of an elemental metal. Chemical reactions between the film and the substrate will usually form two different intermetallic compounds at the contact interface. One way to avoid the occurrence of uncontrolled chemical reactions on compound semiconductors is to deposit a film of an intermetallic compound that is thermodynamically stable with respect to the compound semiconductor.<sup>5,6</sup> Such contacts may offer improved reliability and the ability for devices to operate under harsher environments than is now possible.

Several studies of the Pt-GaAs interface have shown that interdiffusion and chemical reactions occur in the relatively low temperature range of 250 °C–300 °C. Annealing at higher temperatures and/or longer time periods produces a layered structure in which PtAs<sub>2</sub> and Pt-Ga intermetallic compounds such as Pt<sub>3</sub>Ga, Pt<sub>5</sub>Ga<sub>3</sub>, PtGa, and PtGa<sub>2</sub> have been identified.<sup>7–17</sup> The electrical effects of the chemical reactions involving Pt films on GaAs have also been studied.<sup>7–10,14</sup> For both partially and fully reacted samples, the Schottky barrier height tends to increase along with an increase of the ideality factor because of the formation of PtAs<sub>2</sub>, which is a wide band-gap semiconductor.

The ternary phase diagram of Pt-Ga-As, which was determined by Tsai and Williams<sup>18</sup> and by Zheng *et al.*,<sup>19</sup> is presented in Fig. 1. Elemental Pt cannot exist at equilibrium with GaAs, since no tie line connects these two phases. Instead, a closed system that initially contained a large amount of GaAs and a small amount of Pt, e.g., a substrate with a thin film on top, would have a composition that would place it somewhat above GaAs in the phase diagram but below the PtGa-PtAs<sub>2</sub> tie line, as illustrated in Fig. 1. This composition is within the tie-triangle defined by GaAs, PtGa, and PtAs<sub>2</sub>, and thus these compounds, which have been identified in the thin film studies, are the thermodynamically stable phases for the system. The compound Pt<sub>2</sub>Ga is also separated from GaAs by the PtGa-PtAs<sub>2</sub> tie line, so thin films of this compound on GaAs would

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# RHEED studies of epitaxial growth of CoGa on GaAs by MBE – determination of epitaxial phases and orientations

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Epitaxial growth of single crystal CoGa is investigated in-situ using reflection high energy electron diffraction (RHEED). The formation of different phases of CoGa (different stoichiometric compounds and epitaxial orientations) due to various initial growth conditions has been probed with X-ray diffraction and correlated with the RHEED patterns. The growth of (100)CoGa or (110)CoGa is found strongly dependent on the termination of the GaAs surface, with either Co or Ga, before the epitaxial deposition of CoGa. When the flux ratio is deviated from the proper stoichiometric range, additional Co–Ga–As compounds are found in the X-ray diffraction measurement. It is concluded that the CoGa phases and orientations can be determined by pre-deposition of Co or Ga with a control of stoichiometry in the proper range. The high quality epitaxial CoGa has potential applications in thermodynamically stable contacts, and more importantly for fabrication of GaAs/metal/GaAs quantum well structures.

## 1. Introduction

Thermodynamically stable metal contacts on GaAs are very important for both Ohmic and Schottky contacts. Since only W and Mo in the element metal form do not react with GaAs, inter-metallic compounds have attracted great deal of interest in the past few years [1]. These inter-metallic compounds, such as CoGa [2], RhGa [3], NiAl [4], and NiGa [5], have a CsCl structure and the lattice constants are close to half of the lattice constant of GaAs. Thus, epitaxial deposition of these intermetallic compounds on GaAs is plausible.

CoGa has certain advantages which make it a good candidate for metal contact on GaAs. First, there exist only two stable phases of Co/Ga compounds, which are CoGa and CoGa<sub>3</sub> [6], and this makes it easier to control the growth of single phase CoGa on GaAs. Second, the stoichiometry of Co<sub>1-x</sub>Ga<sub>x</sub> can be varied from 31% to 62% [7], and this flexibility of stoichiometric variation makes the flux ratio control less critical. Further-

more, the lattice mismatch of different stoichiometric CoGa's with GaAs (half of the lattice constant), varies from 1.8% to 0.5% as Ga content is adjusted from 31% to 61% [8]. In bulk Co<sub>1-x</sub>Ga<sub>x</sub>, electric and magnetic properties are known to depend on the stoichiometry [9–11]. However, the properties of epitaxial Co<sub>1-x</sub>Ga<sub>x</sub> on GaAs are still relatively unknown. Recent studies by Baugh et al. [12] have shown that the Ga rich condition may be thermodynamically more stable than the Co rich condition. Palmström et al. [2] have demonstrated the growth of CoGa on GaAs and observed the surface reconstruction using reflection high energy electron diffraction (RHEED).

In this paper, we demonstrate the control of growth of single phase CoGa on GaAs and the epitaxial orientation in molecular beam epitaxy (MBE), by controlling the initial growth condition with in-situ RHEED diffraction.

## 2. Experimental

The substrate used in this study was undoped semi-insulating (100)GaAs. The wafer was first degreased, etched in H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O = 8:1:1

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# **Electrical Resistivity, Magnetic Susceptibility and Thermoelectric Power of $\text{PtGa}_2$**

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The electrical resistivity ( $\rho$ ), magnetic susceptibility ( $\chi$ ) and thermoelectric power ( $S$ ) of  $\text{PtGa}_2$  were measured as a function of temperature ( $T$ ). This compound is metallic at high temperatures, as shown from the room-temperature resistivity value ( $19\mu\Omega\text{-cm}$ ) and the linear dependence of the  $S$  vs.  $T$  curve at temperatures above the Debye temperature ( $\theta_D$ ). It undergoes a superconducting phase transition with a critical temperature ( $T_c$ ) at zero magnetic field of 2.13K. The density of states (DOS) at the Fermi energy ( $E_F$ ) at high temperatures obtained from  $\chi$  and  $S$  data are 22% and 15% higher, respectively, than the value obtained previously from a semi-empirical band structure calculation.

**Electronic structure study of the Pt-Ga intermetallic thin films on GaAs (100)  
using X-ray photoemission spectroscopy**

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Single-phase films of Pt-Ga intermetallic compounds with different stoichiometric compositions were grown using molecular beam epitaxy (MBE) and investigated with X-ray photoemission spectroscopy (XPS). For decreasing Pt concentration in the intermetallic compounds, the Pt d-band centroid moved to higher binding energy (BE) and the density of states (DOS) at the Fermi level ( $E_F$ ) decreased. The Pt d-band width narrowed considerably and Pt 4f core level spectra shifted to higher BE as the Pt 4f core level line shape became more symmetric.

# Internal Photoemission in CoGa/GaAs Schottky Barriers, Possible Injection of Electrons into the L Valley

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## ABSTRACT

Internal photoemission in epitaxially grown films of CoGa/GaAs Schottky barriers by back illumination is used to study the injection of electrons into L and X valleys of the conduction bands of n-type GaAs. The general theory of Fowler predicts that the photocurrent per absorbed photon should vary as the square of the photon energy  $h\nu$  for  $[(h\nu - \Phi_b)/kT] \geq 0$ , where  $\Phi_b$  is the difference between the Fermi level and  $\Gamma$  point in the GaAs conduction band. Unlike the case for Au/GaAs Schottky barriers, we observe two thresholds in the photocurrent measurements of uniform epitaxial CoGa/GaAs contacts. The second threshold formed at  $\approx 0.3$  eV higher than the first threshold ( $\Gamma$  point) is interpreted as the injection of carriers into the L valley of the GaAs from the metal side. A third threshold at  $\approx 0.5$  eV above the  $\Gamma$  point requires a photon energy greater than the energy gap of GaAs (1.4 eV) and hence cannot be observed in the back illumination mode.

## INITIAL STAGES OF METAL/SEMICONDUCTOR INTERFACE FORMATION: Au AND Ag ON Si(111)

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We have studied the atomic structures formed by monolayer coverages of Au and Ag on the Si(111) surface using primarily the technique of impact-collision ion scattering spectroscopy (ICISS). For the case of Au films annealed at 700°C, three different types of LEED patterns are formed depending on the fractional monolayer coverage:  $5 \times 1$ ,  $\sqrt{3} \times \sqrt{3}$ , and  $6 \times 6$ . The ICISS data reveal that all the three surfaces are structurally similar: the Au atoms reside above the Si(111) plane, most likely in threefold-hollow sites, and the different surfaces appear to be characterized by rows ( $5 \times 1$ ) or a honeycomb network ( $\sqrt{3} \times \sqrt{3}$  and  $6 \times 6$ ). In contrast, the Ag films deposited at elevated substrate temperature (480°C) display only a  $\sqrt{3} \times \sqrt{3}$  LEED pattern for coverages ranging from 0.25 to 35 monolayers. A trimer model appears to be more consistent with the low coverage Ag ICISS data rather than a honeycomb arrangement of the Ag atoms.

### 1. Introduction

The reconstructions induced on the Si(111) surface by the noble metals Au and Ag have been the subjects of many scientific investigations for a great many years [1,2], but as yet there is no consensus on their detailed atomic structures. If anything, the number of proposed structural models has increased in proportion to the number of studies. This is principally because each of the currently utilized surface structure techniques is sensitive to a different aspect of the surface structure. One might think that the most direct real-space technique, scanning tunneling microscopy (STM), would resolve any ambiguities. However, as demonstrated last year by two consecutive papers in Physical Review Letters on the Ag-induced  $\sqrt{3} \times \sqrt{3}$  Si(111) surface [3,4], STM is not yet capable of elemental recognition. Although both papers showed essentially identical honeycomb patterns, one group concluded that the STM features were caused by Si adatoms atop Ag trimers [3] and the other decided that the STM features were individual Ag adatoms [4]. A recent X-ray diffraction study concluded that this surface

was characterized by Ag trimers, but without Si adatoms above the trimers [5]. An STM study of a surface that might be structurally similar, that is the Au-induced  $\sqrt{3} \times \sqrt{3}$  Si(111) surface, revealed triangular shaped features that were interpreted to be Au trimers [6], although later work showed the features to be essentially circular [7]. Our previous impact-collision ion scattering spectroscopy (ICISS) [8] studies of Au:  $\sqrt{3} \times \sqrt{3}$  Si(111) were shown to be consistent with a honeycomb structure [9].

Ion scattering techniques do not directly image a surface, but they do have several advantages for structural analysis: the data provide real-space information (i.e. no diffraction), the scattering features are determined by the nuclear positions (not the valence electrons), and the scattered-ion energy depends on the mass of the scattering atom (elemental specificity). In this paper, we will review the bases of our conclusions regarding the structure of the Au-induced Si(111) reconstructions and argue that a honeycomb model is consistent with the published STM images [6]. We also present ICISS data for the Ag-induced  $\sqrt{3} \times \sqrt{3}$  Si(111) surface, and conclude that the